ISSN 1063-7850, Technical Physics Letters, 2013, Vol. 39, No. 4, pp. 377–379. © Pleiades Publishing, Ltd., 2013.
Original Russian Text © V.V. Osipov, V.I. Solomonov, S.F. Konev, S.O. Cholakh, 2013, published in Pis'ma v Zhurnal Tekhnicheskoi Fiziki, 2013, Vol. 39, No. 8, pp. 40–46.

Trivalent Zirconium and Hafnium Ions in Yttria-Based Transparent Ceramics

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Received December 5, 2012

Abstract—Electron paramagnetic resonance spectra of transparent yttria-based ceramics with zirconium and hafnium additives contain signals with close parameters due to paramagnetic Zr^{3+} and Hf^{3+} ions, which have similar ground-state electron configurations of [Kr]$4d^1$ and [Xe]$5d^1$, respectively.

DOI: 10.1134/S1063785013040214

During the synthesis of ceramics based on Y_2O_3 (yttria), it is common practice to use dioxides of tetravalent ions (ThO_2, ZrO_2, HfO_2) as sintering additives, which simultaneously favor an increase in the transparency of ceramics. In particular, Yttralox—a ceramic material created by General Electric Co. (United States)—consists of 90 mol % Y_2O_3 and 10 mol % ThO_2 and is close to glass with respect to transmission in the visible spectral range [1]. Russian specialists [2, 3] have developed a technology of yttria-based ceramics with additives of 10 mol % ZrO_2 or HfO_2, which are characterized by a transmission of 86 or 82%, respectively, at a wavelength of 6 μm. These ceramics are used in bulbs for high-pressure lamps of elevated brightness.

Ceramics activated by rare-earth ions can also be used as active elements of solid-state lasers. Highly transparent modified Yttralox ceramics (Y_2O_3 with additives of 10 mol % ThO_2 and 1 mol % Nd_2O_3) [4] was used to create the first polycrystalline ceramic lasers [5], although their efficiency was relatively low. Investigations aimed at creating more effective laser ceramics were continued, and new yttria-based compositions with ZrO_2 and HfO_2 additives were created [6–8]. It was found [7] that the optimum ZrO_2 content in these ceramics for highly effective lasing is about 3 mol %. However, it was a priori believed that additive metal ions (Th, Zr, Hf) occur in the lattice in tetravalent states not forming centers of luminescence and absorption.

In recent years, ZrO_2 and HfO_2 additives have been introduced into yttria activated by rare-earth ions in order to produce disordering of the crystal structure of ceramic grains, which ensures broadening of the amplification band of activator ions. These ceramics are promising materials for the active media of lasers generating ultrashort radiation pulses. In particular, it was shown [8, 9] that the introduction of 12 mol % ZrO_2 and 24 mol % Lu_2O_3 unto neodymium-activated yttria led to broadening of lasing transition in Nd^{3+} ions up to 40 nm. The transmission of this ceramics in the region of lasing ($\lambda = 1.03–1.07$ μm) reached 81.6%. However, attempts at obtaining laser generation in neodymium-activated ceramics with a composition of $[(Nd_{0.01}Y_{0.99})_2O_3]_{0.88}(ZrO_2)_{0.12}$ were unsuccessful. Lasing at $\lambda = 1.034$ μm was obtained in ytterbium-activated ceramics with a composition of $[(Yb_{0.01}Y_{0.99})_2O_3]_{0.88}(ZrO_2)_{0.12}$ [9], but the optical efficiency was lower than that in zirconia-free ceramics of $(Yb_{0.01}Y_{0.99})_2O_3$ [10]. One possible explanation of these facts is that trivalent Zr^{3+} ions present in zirconia-containing ceramics form additional channels of laser level quenching, e.g., via dipole–dipole interaction. This hypothesis is confirmed by a decrease in the effective lifetime of the upper laser level of Nd^{3+} ion in ceramics with a composition of $[(Nd_{0.01}Y_{0.99})_2O_3]_{0.88}(ZrO_2)_{0.12}$ as compared to that in the analogous zirconia-free ceramics [9]. However, to the best of the authors' knowledge, no data were reported on the possible presence of trivalent zirconium and hafnium ions in high-transparency yttria-based ceramics with additives of these elements.

The aim of the present work was to use the electron paramagnetic resonance (EPR) method for determining the presence of trivalent zirconium and hafnium ions in high-transparency yttria-based ceramics.

We have studied the samples of ceramics with the following compositions: $(Y_2O_3)_{0.94}(HfO_2)_{0.06}$ (sample 1), $(Y_2O_3)_{0.94}(ZrO_2)_{0.06}$ (sample 2), $[(Y_2O_3)_{0.94}(ZrO_2)_{0.06}]_{0.94}(HfO_2)_{0.06}$ (sample 3), and Y_2O_3 (sample 4). All samples were not activated by rare-earth ions in order to obtain EPR spectra not distorted by these paramagnetic centers. The ceramics

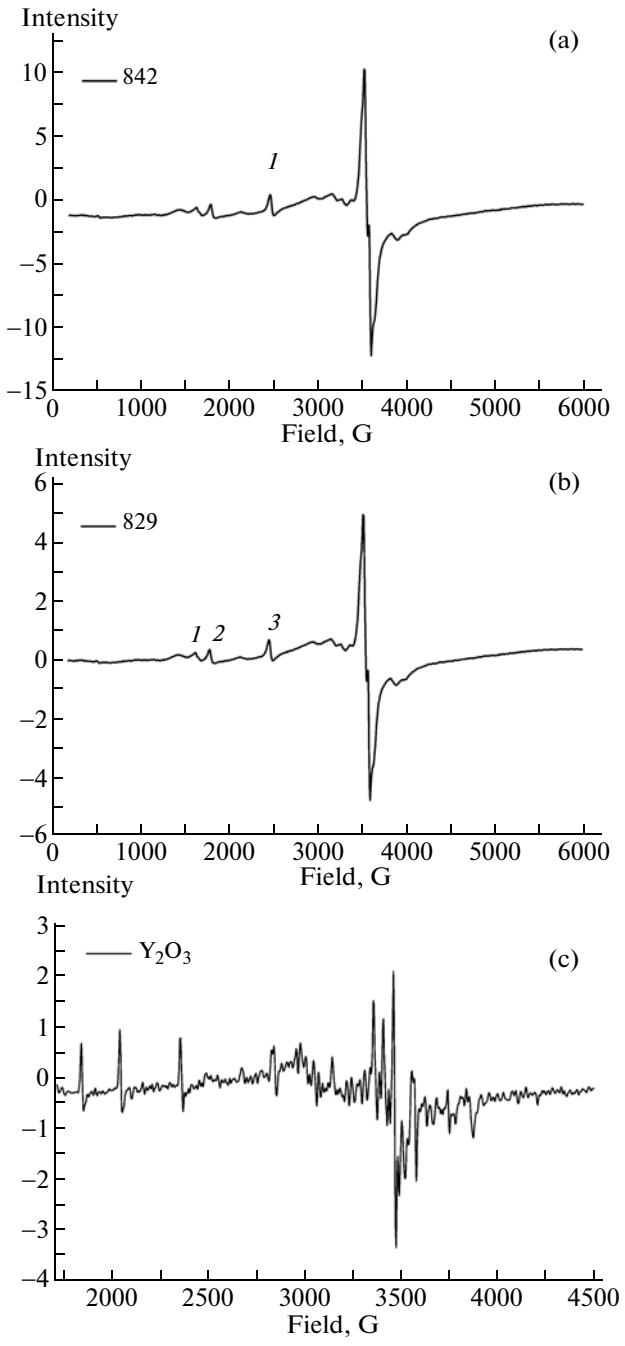

Fig. 1. EPR spectra of (a) $(Y_2O_3)_{0.94}(HfO_2)_{0.06}$, (b) $(Y_2O_3)_{0.94}(ZrO_2)_{0.06}$, and (c) "pure" Y_2O_3 (sample 4).

were manufactured from nanopowders of components, which were prepared by laser synthesis techniques [11]. The content of uncontrolled impurities did not exceed 0.001%. The samples of transparent ceramics were sintered at 1950°C for 10 h in a vacuum furnace with tungsten heaters. The X-ray diffraction (XRD) measurements on a D8 Discovery diffractometer showed that all samples represented solid solutions of additives in a cubic Y_2O_3 phase. The EPR measurements were performed on a Bruker ELEXSYS E580 instrument with a resonance frequency of ν_r = 9.27 GHz in the interval of magnetic induction variation from 200 to 6000 G.

Figures 1a and 1b show the EPR spectra of yttria-based ceramics with hafnia and zirconia additives, which are very similar to each other in the region of B = 2400–3700 G. Data on the parameters of EPR spectra of the ceramics studied are presented in the table. The EPR spectra of ceramics with additives significantly differ from the spectrum of freshly cleaved "pure" yttria ceramics (Fig. 1c), which only displays weak signals of paramagnetic centers that appear as a result of mechanical cleavage of this sample.

As is known, Y^{3+}, O^{2-}, Zr^{4+}, and Hf^{4+} ions possess closed outer electron shells and cannot be manifested in the EPR spectrum. Therefore, the EPR signals observed in the region of B = 2400–3700 G for the samples of ceramics containing zirconia and hafnia should be assigned to the presence of paramagnetic trivalent Zr^{3+} and Hf^{3+} ions. These ions possess similar ground-state electron configurations of $[Kr]4d^1$ (Zr^{3+}) and $[Xe]5d^1$ (Hf^{3+}). In the spectra of crystals, these electron configurations form an orbital doublet (E) and triplet (T_2) separated by a value equal to the crystal field strength ($10Dq$), In the same crystal fields, Zr^{3+} and Hf^{3+} ions exhibit almost identical structures of energy levels and approximately the same Zeeman splitting in external magnetic field. Both ions exhibit a hyperfine structure in the EPR spectrum, which is indicative of the interaction between the spin of unpaired electron and magnetic field of the nucleus (in native zirconium, 77% of isotopes possess a nuclear spin of $I = 0$ and the remaining 23% of isotopes possess a nuclear spin of $I = 5/2$; in native hafnium, about 68% of isotopes possess a nuclear spin of $I = 0$, 18% of isotopes possess a nuclear spin of $I = 7/2$, and 14% of isotopes possess a nuclear spin of $I = 9/2$).

The appearance of zirconium and hafnium ions in trivalent states in Y_2O_3 is quite possible. Indeed, in the cubic lattice of Y_2O_3, tetravalent Zr^{4+} (Hf^{4+}) ions replace the host Y^{3+} cations situated at the center of the YO_6 cube. In one-third of these cubes, the natural oxygen vacancies occur at the vertices on the face diagonal [12], while in the other two-thirds of cubes these vacancies occur on the spatial diagonal [12]. When zirconium (hafnium) ions in tetravalent states enter into Y_2O_3, their electric charge can be compensated by transformation of the YO_6 cubes into $Zr(Hf)O_8$ cubes due to displacements of oxygen ions from the neighboring cubes. As a result, a certain portion of these cubes transform into distorted tetrahedra, in which Zr^{3+} (Hf^{3+}) can be arranged. The distortion of the crystal field can produce a weak splitting of the lower levels (E) in these ions, which will lead to the appearance of signals with g-factors above $g = 2$ in the EPR spectra. These Zr^{3+} (Hf^{3+}) can act as acceptors

Parameters of the EPR spectra of yttria-based ceramics with hafnia and zirconia additives

Sample no. (additive)	*g*-factor	Linewidth ΔB, G	Intensity
1	2.83856	45.1	1.83
(Hf)	1.9909	32.0	3.00
	1.98886	118.0	6.00
	1.97219	21.0	6.00
2	4.2066	63.3	0.27
(Zr)	3.86555	55.5	0.46
	2.8345	41.6	0.70
	1.9979	35.0	2.00
	1.9916	98.0	2.20
	1.9713	15.0	1.50
3	4.20504	66.7	0.59
(Zr + Hf)	2.82777	68.0	0.19
	1.98577	90.0	1.40
	1.9827		0.40
	1.9712		0.40

with respect to activator ions (Nd^{3+}, Yb^{3+}) in laser ceramics, thus producing additional quenching of the upper laser levels.

Thus, it has been demonstrated that, in a solid solution based on Y_2O_3 with hafnia and zirconia additives, a certain fraction of zirconium and hafnium impurity ions can occur in the trivalent state.

Acknowledgments. This study was supported in part by programs of the Presidium of the Russian Academy of Sciences (project no. 12-P-2-1011), the Presidium of the Ural Branch of the Russian Academy of Sciences (project no. 12-2-003-YaTs), and the Russian Foundation for Basic Research (project no. 13-08-00159).

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Translated by P. Pozdeev